CLASSIFICATION SECRET

50X1-HUM

CENTRAL INTELLIGENCE AGENCY
INFORMATION FROM
FOREIGN DOCUMENTS OR RADIO BROADCASTS

REPORT

CD NO.

COUNTRY	USSR	DATE OF INFORMATION	1949
SUBJECT	Scientific - Chemistry	DATE DIST.	3 Jan 1951
HOW PUBLISHED	Thrice-monthly periodical		
WHERE PUBLISHED	Moscow-Leningrad	NO. OF PAGES	4
DATE PUBLISHED	11 Jul 1949	SUPPLEMENT TO REPORT NO.	
LANGUAGE	Russian		

THIS IS UNEVALUATED INFORMATION

SOURCE Doklady Akademii Nauk SSSR Vol LXVII, No 2, 1949, pp 293-295.

FORMATION OF THE PHOSPHORUS-CARBON BOND IN THE COUPLED REACTION OF HYDROCARBONS, PHOSPHORUS TRICHLORIDE, AND OXYGEN

L. Z. Soborovskiy,
Yu. M. Zinov'yev,
and M. A. Englin
Presented by
Acad A. N. Nesmeyanov
3 May 1949

/The reactions described here suggest an attempt either to modify and improve the first step of the "GE" synthesis, or to synthesize similar compounds. Although the absence of experimental results on ethane is not explained, the reason may be the comparative difficulty of formation of a P-C bond at a primary carbon atom. Derivatives containing a chlorine atom in the alkyl group may conceivably serve as intermediates in the synthesis of new substances having a higher toxicity and lower volatility than known compounds. The reasons which prompted the USSR investigators to launch the investigation in question have not been stated by them. The reactions studied are quite general. Under the circumstances, the references to potential applications in experimental work on nerve poisons are purely conjectural and express objective possibilities only./

Up to the present, only one example of the direct interaction of phosphorus trichloride with a hydrocarbon has been known: the reaction between benzene and PCl_3 described by A. Ye. Arbuzov (1) and Michaelis (2). This reaction proceeds only at a very high temperature and is achieved by passing a mixture of the vapors of benzene and phosphorus trichloride through a red-hot procelain or glass tube.

Results of the study of the interaction of phosphorus trichloride with various hydrocarbons are cited in the present report: paraffins, cycloparaffins, olefins, and certain of their derivatives (NOTE: In December 1948 a paper by Clayton and Jensen was published (3), in which the reaction of certain hydrocarbons with phosphorus trichloride was also described.

STATE	X	NAVY	X	NSRB		DISTRIBUTION											
ARMY	X	AIR	X	FBI													

50X1-HUM

It was established that phosphorus trichloride in conditions where the presence of oxygen is excluded does not react with hydrocarbons to form compounds containing the phosphorus-carbon bond as it does in the cold and at temperatures less than 350-400°. This process also is not stimulated by intensive exposure of the reactive mixture to a mercury-quartz lamp.

Similarly, no noticeable reaction forming the phosphorus-carbon bond develops from the interaction of hydrocarbons with pure phosphorus oxychloride either in the presence or in the absence of oxygen.

However, through the simultaneous interaction of phosphorus trichloride, a hydrocarbon, and oxygen there takes place extremely easily and smoothly, at ordinary temperatures, the formation of a phosphorus-carbon bond in a reaction in which chlorides of alkylphosphonic acids ($RPOCl_2$), hydrogen chloride, and phosphorus oxychloride are formed.

The above reaction was studied in detail in the case of the paraffin series of hydrocarbons, in particular: isobutane, pentane, isopentane, 2, 3-dimethylbutane, hexane, cyclohexane, heptane, and 2, 2, 4-trimethylpentane (iso-octane). The respective chlorides of alkylphosphonic acids were isolated and described.

This unique reaction should be considered as a coupled oxidation of phosphorus trichloride and the hydrocarbon, leading to the formation of the phosphorus-carbon bond and phosphorus oxychloride.

Taking into account that paraffin and cycloparaffin hydrocarbons are practically not oxidized under ordinary conditions by oxygen, it is possible to assume that the reactions described commence with the process of oxidation of phosphorus trichloride, which takes place easily and brings about the coupled oxidation of the hydrocarbon. This process in all probability is accompanied by the formation of free radicals, and this leads to the formation of the phosphorus-carbon bond.

The reactions in question can be represented by the following overall scheme:

$$2\,PCl_3 + R\text{-}H + O_2 \longrightarrow RPOCl_2 + POCl_3 + HCl$$

Like the paraffin hydrocarbons, the olefins do not enter into reaction with phosphorus trichloride in the absence of oxygen, or with phosphorus oxychloride either in the absence or in the presence of oxygen.

As a result of the interaction of ethylene hydrocarbons, phosphorus trichloride, and oxygen, chlorides of the chloralkylphosphonic acids and phosphorus oxychloride are obtained. No evolution of hydrogen chloride was observed in this reaction.

These facts lead to the assumption that the same mechanism of the reactions in question is common to both the paraffin and the olefin hydrocarbons.

The reactions with olefins can be expressed by the following overall scheme:

$$RCH = CH_2 + PCl_3 + O_2 \longrightarrow RC_2H_3ClPOCl_2 + POCl_3$$

Reactions were achieved with the following olefins: ethylene, propylene, butylene, and isobutylene. The properties of the chlorides of chloralkylphosphonic acids thus obtained are cited in Table 1. The study of the products of reaction with octylene and styrene were greatly complicated by the considerable polymerization of these compounds under the conditions of the reaction.

We also studied the new synthesis described for organic phosphorus compounds, using certain hydrocarbon derivatives, particularly dichlorethane, chloroform, acetonitrile, and nitromethane.

SECRET

It was found that dichlorethane and chloroform, when they react with phosphorus trichloride in the presence of oxygen, produce small yields of the respective organic phosphorus compounds. Both acetonitrile and nitromethane not only do not react with phosphorus trichloride, but also impede the oxidation of the latter into the oxychloride. However, the presence of acetonitrile or nitromethane does not disturb the reaction between a hydrocarbon, phosphorus trichloride, and oxygen which results in the formation of corresponding chlorides of alkylphosphonic acids and phosphorus oxychloride. Benzene does not enter into reaction with phosphorus trichloride under the conditions described.

In all cases the experiments were conducted in a glass reaction vessel provided with a reflux condenser, a gas-conducting tube with a porous disk, and a thermometer.

Phosphorus trichloride and the liquid hydrocarbon were placed into the reaction vessel and oxygen was fed into the mixture at a rate of about 2 litres per hour. The reaction was accompanied by an evolution of heat, and the temperature of the reaction mixture rose from 20° to 40-70°, depending on the hydrocarbon used. The process ended after the reaction mixture stopped heating up. The reactions with gaseous hydrocarbons were accomplished by passing the mixture of hydrocarbon and oxygen into phosphorus trichloride which was placed into the reaction vessel.

At the conclusion of the reaction the phosphorus trichloride and hydrocarbon which had not reacted and also phosphorus oxychloride were distilled off. The residue with a high boiling point was then distilled in vacuum. The yield of chlorides of alkyl- and chloralkylphosphonic acids reached 55-60% of the theoretical, on the basis of the hydrocarbon which had reacted (except for the chloride of chlorethylphosphonic acid, whose yield was insignificant).

The properties of the chlorides of alkyl- and chloralkylphosphonic acids which were synthesized in the above manner are noted in Table 1.

Presented 29 April 1949

References

1. A. Ye. Arbuzov, On the Phenomena of Catalysis in the Field of Certain Phosphorus Compounds (O Yavleniyakh kataliza v oblasti nekotorykh soyedineniy fosfora), 1914.

2. A. Michaelis, Ann, 181, 265 (1876).

3. J. O. Clayton and W. L. Jensen, Jour Am Chem Soc, 70, 3880 (1948)

[Table 1 follows.]

SECRET

Table 1. Properties of Synthesized Chlorides of Alkyl- and Chloralkylphosphonic Acids

Initial Hydrocarbon	Formula of Dichloroxy Phosphine Obtained	Boiling Point in °C/mm Hg	Specific Gravity	Index of Refraction	Molecular Refraction Found	Molecular Refraction Calculated
A. Paraffins						
Isobutane	$i\text{-}C_4H_9POCl_2$	55-57/2	1.2639	1.4660	38.34	38.72
n-Pentane	$C_5H_{11}POCl_2$	67-69/2	1.2180	1.4694	43.06	43.34
2-Methylbutane	$i\text{-}C_5H_{11}POCl_2$	64-65.5/2	1.2246	1.4708	43.12	43.34
n-Hexane	$C_6H_{13}POCl_2$	82-84/3	--	--	--	--
2, 3 Dimethylbutane	$i\text{-}C_6H_{13}POCl_2$	75-76/2	1.1733	1.4715	48.40	47.96
Cyclohexane	$C_6H_{11}POCl_2$	93-94/2	Melt. pt. 39-40°	--	--	--
n-Heptane	$C_7H_{15}POCl_2$	96-98/2	1.1852	1.4830	52.30	52.58
2, 2, 4-Trimethylpentane	$i\text{-}C_8H_{17}POCl_2$	81-82/2	1.1329	1.4707	56.97	57.20
B. Olefins						
Ethylene	$CH_2ClCH_2POCl_2$	86.5-87/2	1.5446	1.4998	34.58	34.36
Propylene	$C_3H_6ClPOCl_2$	85-87/2	1.4615	1.4930	38.85	38.97
Butylene	$C_4H_8ClPOCl_2$	85-87/5	1.3950	1.4900	43.40	43.65
Isobutylene*	$i\text{-}C_4H_8ClPOCl_2$	78-80/4	--	--	--	--

*The product of reaction contained an admixture of polymers of isobutylene which could not be eliminated. Therefore the value for specific weight and for the index of refraction are not given for chlorisobutylphosphonic acid.

- E N D -

SECRET

SECRET

SECRET

50X1-HUM